

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 867 415 A2

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
30.09.1998 Bulletin 1998/40

(51) Int Cl.<sup>6</sup>: C03C 4/08, C03C 4/02,  
C03C 3/095

(21) Application number: 98302263.3

(22) Date of filing: 25.03.1998

(84) Designated Contracting States:  
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 26.03.1997 JP 73025/97

(71) Applicant: NIPPON SHEET GLASS CO. LTD.  
Chuo-ku Osaka-shi Osaka-fu (JP)

(72) Inventors:  
• Nagashima, Yukihito  
Chuo-ku, Osaka-shi, Osaka (JP)

• Takatsuki, Nobuyuki  
Chuo-ku, Osaka-shi, Osaka (JP)  
• Kuroda, Isamu  
Chuo-ku, Osaka-shi, Osaka (JP)

(74) Representative: Carpenter, David et al  
MARKS & CLERK,  
Alpha Tower,  
Suffolk Street Queensway  
Birmingham B1 1TT (GB)

(54) Ultraviolet and infrared radiation absorbing glass

(57) An ultraviolet and infrared radiation absorbing  
glass is disclosed, comprising, in % by weight:  
basic glass components comprising

65 to 80% SiO<sub>2</sub>,  
0 to 5% Al<sub>2</sub>O<sub>3</sub>,  
0 to 10% MgO,  
5 to 15% CaO,  
10 to 18% Na<sub>2</sub>O,  
0 to 5% K<sub>2</sub>O,  
5 to 15% MgO + CaO,  
10 to 20% Na<sub>2</sub>O + K<sub>2</sub>O,

0 to 5% B<sub>2</sub>O<sub>3</sub>, and  
SO<sub>3</sub>, and

coloring components comprising

0.40 to 0.90% total iron oxide (T-Fe<sub>2</sub>O<sub>3</sub>) in terms of  
Fe<sub>2</sub>O<sub>3</sub>,  
1.0 to 2.0% CeO<sub>2</sub>, and  
0 to 1.0% TiO<sub>2</sub>,

with 27 to 40% of said T-Fe<sub>2</sub>O<sub>3</sub> being FeO in terms of  
Fe<sub>2</sub>O<sub>3</sub>. The SO<sub>3</sub> is present in the range of 0.07 to 0.18%.

EP 0 867 415 A2

## Description

FIELD OF THE INVENTION

5 The present invention relates to an ultraviolet and infrared radiation absorbing glass having a green tint. More particularly, the present invention relates to an ultraviolet and infrared radiation absorbing glass for use as a glass for automobiles.

BACKGROUND OF THE INVENTION

10 In recent years, the interior trim of automobiles tends to be luxury, and to cope with the demand for the protection of the interior trim from deterioration and to reduce the load of air conditioning, a green-tinted glass having ultraviolet and infrared radiation absorbing power imparted thereto has been proposed as window glass of automobiles.

15 For example, glass having an ultraviolet transmission reduced to about 38% or less, a total solar energy transmission limited to about 46% or less and a visible light transmission of at least 70% for ensuring the vision from the inside of an automobile, is known. Further, there is a recent trend that a bluish green tint is preferred for such a green-tinted glass for automobiles.

20 It is known that the total solar energy transmission can be decreased by increasing the absolute amount of ferrous oxide (FeO) out of the iron oxides introduced into the glass, and almost all of conventional infrared radiation absorbing glasses use this method.

25 On the other hand, various methods have hitherto been proposed on a method for decreasing an ultraviolet transmission. For example, JP-A-6-56466 (the term "JP-A" as used herein means an "unexamined published Japanese patent application") discloses an ultraviolet radiation absorbing glass having a green tint, which comprises a soda-lime-silica basic glass composition having incorporated therein, as coloring components, 0.53 to 0.70% of total iron oxides in terms of  $\text{Fe}_2\text{O}_3$ , 0.5 to 0.8% of  $\text{CeO}_2$ , 0.2 to 0.4% of  $\text{TiO}_2$ , and 30 to 40% of FeO in terms of  $\text{Fe}_2\text{O}_3$  based on the total iron oxides in terms of  $\text{Fe}_2\text{O}_3$ .

30 JP-B-6-2812 (the term "JP-B" as used herein means an "examined Japanese patent publication") discloses an ultraviolet radiation absorbing glass having a green tint, which comprises, in % by weight, a basic glass composition comprising 65 to 75% of  $\text{SiO}_2$ , 0 to 3% of  $\text{Al}_2\text{O}_3$ , 1 to 5% of  $\text{MgO}$ , 5 to 15% of  $\text{CaO}$ , 10 to 15% of  $\text{Na}_2\text{O}$ , and 0 to 4% of  $\text{K}_2\text{O}$ , and coloring components comprising 0.65 to 1.25% of total iron oxides in terms of  $\text{Fe}_2\text{O}_3$ , 0.2 to 1.4% or 0.1 to 1.36% of  $\text{CeO}_2$  and 0.02 to 0.85% of  $\text{TiO}_2$ .

35 JP-A-6-208266 discloses an ultraviolet and infrared radiation absorbing glass having a green tint, which comprises a soda-lime glass having incorporated therein 0.52 to 0.63% of total iron oxides in terms of  $\text{Fe}_2\text{O}_3$ , 0.9 to 2% of  $\text{CeO}_2$ , 0.2 to 0.6% of  $\text{TiO}_2$  and 0 to 0.002% of  $\text{CoO}$ , as coloring components.

Since cerium oxide is expensive, an ultraviolet and infrared radiation absorbing glass having decreased cerium oxide content has also been proposed.

40 For example, JP-A-4-231347 describes a green-tinted ultraviolet radiation absorbing glass, which comprises a soda-lime-silica basic glass composition having incorporated therein, as coloring components, more than 0.85% by weight of total iron oxide (T- $\text{Fe}_2\text{O}_3$ ) in terms of  $\text{Fe}_2\text{O}_3$ , with the  $\text{FeO/T-Fe}_2\text{O}_3$  ratio being less than 0.275, and less than 0.5% by weight of  $\text{CeO}_2$ .

JP-A-6-191881 discloses an ultraviolet radiation absorbing glass having a pale green tint, which comprises a soda-lime-silica basic glass composition having incorporated therein a coloring agent part comprising less than 2.0% of  $\text{TiO}_2$  and more than 0.6% of total iron oxide (T- $\text{Fe}_2\text{O}_3$ ) in terms of  $\text{Fe}_2\text{O}_3$  with the  $\text{FeO/T-Fe}_2\text{O}_3$  ratio being less than 0.35.

45 JP-B-7-121815 discloses an ultraviolet radiation absorbing green glass, which comprises a soda-lime glass having incorporated therein 0.7 to 0.95% of total iron oxide in terms of  $\text{Fe}_2\text{O}_3$  and 0.19 to 0.24% of FeO. In this case, it is very important that the  $\text{SO}_3$  content is within an extremely narrow range of from 0.20 to 0.25% by weight.

50 In the above-described conventional ultraviolet and infrared radiation absorbing glasses, the ultraviolet absorbing power is imparted by the ultraviolet absorption of  $\text{Fe}_2\text{O}_3$ ,  $\text{CeO}_2$  and  $\text{TiO}_2$  individually or by the interaction thereof. Of these components, the ultraviolet absorption of  $\text{Fe}_2\text{O}_3$  or the ultraviolet absorption by the interaction between  $\text{TiO}_2$  and FeO extends to the visible region. Accordingly, when the glass is designed to have an increased ultraviolet absorption, the visible light transmission in the short wavelength region is simultaneously lowered and as a result, the glass comes to have a yellowish tint. Therefore, in order to enhance the ultraviolet absorbing power without giving a yellowish tint which is not preferred as a glass for automobiles, the composition must have a large  $\text{CeO}_2$  content.

55 However,  $\text{Fe}_2\text{O}_3$  and  $\text{CeO}_2$  are an oxidizing agent and when these are contained in a large amount, it is very difficult to obtain a glass which has an oxidation-reduction equilibrium of iron oxide shifted to the reduction side and thus contains a large amount of FeO to thereby exhibit excellent infrared absorption. More specifically, in order to cancel the oxidation action of  $\text{Fe}_2\text{O}_3$  and  $\text{CeO}_2$  and shift the oxidation-reduction equilibrium of the iron oxide to the reduction side more than usual, a reducing agent must be added to a batch in a larger amount than usual. This en-

courages decomposition of the salt cake (sodium sulfate) which accelerates melting of the batch, particularly, melting of the quartz sand, as a result, not only the solubility of batch, particularly, of quartz sand is worsened to cause extreme reduction in the melting capacity but also floating of undissolved quartz sand (so-called scum) may be generated or a ream defect having a larger silica content (so-called silica-rich ream) may come out on the surface.

## SUMMARY OF THE INVENTION

The present invention has been made in the light of the above-described problems encountered in the conventional techniques.

Accordingly, an object of the present invention is to provide an ultraviolet and infrared radiation absorbing glass free from a yellowish tint which is not preferred as a glass for automobiles and having excellent ultraviolet and infrared absorbing power, in a high productivity without causing extreme reduction in the melting capacity or in the yield due to scum or reams.

The ultraviolet and infrared radiation absorbing glass of the present invention comprises, in % by weight of said glass:

basic glass components comprising:

65 to 90%  $\text{SiO}_2$ ,  
 0 to 5%  $\text{Al}_2\text{O}_3$ ,  
 0 to 10%  $\text{MgO}$ ,  
 5 to 15%  $\text{CaO}$ ,  
 10 to 18%  $\text{Na}_2\text{O}$ ,  
 0 to 5%  $\text{K}_2\text{O}$ ,  
 5 to 15%  $\text{MgO} + \text{CaO}$ ,  
 10 to 20%  $\text{Na}_2\text{O} + \text{K}_2\text{O}$ ,  
 0 to 5% of  $\text{B}_2\text{O}_3$ , and  
 $\text{SO}_3$ , and

coloring components,  
 characterised in that the  $\text{SO}_3$  is present in the range of 0.07 to 0.18%, and in that the coloring components comprise in wt% of said glass

0.40 to 0.90% total iron oxide (T- $\text{Fe}_2\text{O}_3$ ) in terms of  $\text{Fe}_2\text{O}_3$ ,  
 1.0 to 2.0%  $\text{CeO}_2$ , and  
 0 to 1.0%  $\text{TiO}_2$ ,

with 27 to 40% of said T- $\text{Fe}_2\text{O}_3$  being FeO in terms of  $\text{Fe}_2\text{O}_3$ .

In the ultraviolet and infrared radiation absorbing glass of the present invention, the basic glass component preferably comprise 0.07 to 0.14% by weight of  $\text{SO}_3$ .

The ultraviolet and infrared radiation absorbing glass of the present invention preferably comprises, when the glass has a thickness of 4.75 to 6.25 mm, 0.40 to 0.60% by weight of total iron oxide (T- $\text{Fe}_2\text{O}_3$ ) in terms of  $\text{Fe}_2\text{O}_3$ .

The ultraviolet and infrared radiation absorbing glass of the present invention preferably comprises, when the glass has a thickness of 3.25 to 4.25 mm, 0.60 to 0.90% by weight of total iron oxide (T- $\text{Fe}_2\text{O}_3$ ) in terms of  $\text{Fe}_2\text{O}_3$ .

In any cases, the ultraviolet and infrared radiation absorbing glass of the present invention preferably comprises 1.45 to 2.0% by weight of  $\text{CeO}_2$ .

Further, FeO in terms of  $\text{Fe}_2\text{O}_3$  preferably occupies 30 to 40% of the T- $\text{Fe}_2\text{O}_3$ .

The ultraviolet and infrared radiation absorbing glass of the present invention preferably has, when the glass has a thickness of 3.25 to 6.25 mm, optical characteristics such that a visible light transmission determined with CIE standard illuminant A is 70% or more, a solar energy transmission is less than 50%, an ultraviolet transmission defined by ISO 9050 is 10% or less, and a dominant wavelength determined with CIE standard illuminant C is 495 to 535 nm.

## DETAILED DESCRIPTION OF THE INVENTION

The reasons for limitations of the glass composition of the ultraviolet and infrared radiation absorbing glass according to the present invention are described below. Hereinafter, all percents are by weight.

$\text{SiO}_2$  is a main component of forming a skeleton of glass. If the  $\text{SiO}_2$  content is less than 65%, the glass has poor

durability, whereas if it exceeds 80%, it is difficult to melt the glass composition.

$\text{Al}_2\text{O}_3$  is a component of improving durability of glass. However, if the  $\text{Al}_2\text{O}_3$  content exceeds 5%, it is difficult to melt the glass composition. The  $\text{Al}_2\text{O}_3$  glass content is preferably from 0.1 to 2%.

$\text{MgO}$  and  $\text{CaO}$  are used to improve durability of glass and at the same time to control liquidus temperature and viscosity of glass composition in forming a glass. If the  $\text{MgO}$  content exceeds 10%, the liquidus temperature rises. If the  $\text{CaO}$  content is less than 5% or exceeds 15%, the liquidus temperature rises. If the total content of  $\text{MgO}$  and  $\text{CaO}$  is less than 5%, durability of the glass lowers, and if it exceeds 15%, the liquidus temperature rises.

$\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  are used as a glass melting accelerator. If the  $\text{Na}_2\text{O}$  content is less than 10% or if the total content of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  is less than 10%, the effect of melting acceleration is poor. If the  $\text{Na}_2\text{O}$  content exceeds 18% or if the total content of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  exceeds 20%, durability of the glass decreases. The  $\text{K}_2\text{O}$  content preferably does not exceed 5% because  $\text{K}_2\text{O}$  is expensive as compared with  $\text{Na}_2\text{O}$ .

$\text{B}_2\text{O}_3$  is a component used for improving durability of the glass or as a melting aid, but it also has a function of enhancing the ultraviolet absorption. If the  $\text{B}_2\text{O}_3$  content exceeds 5%, decrease of the transmission in the ultraviolet region extends to the visible region. As a result, not only the tint tends to be yellowish, but also disadvantages occur in forming a glass due to volatilization of  $\text{B}_2\text{O}_3$  and the like. Accordingly, the upper limit of the  $\text{B}_2\text{O}_3$  content is 5%.

The iron oxide is present in the glass in the form of  $\text{Fe}_2\text{O}_3$  and  $\text{FeO}$ .  $\text{Fe}_2\text{O}_3$  is a component of enhancing the ultraviolet absorbing power together with  $\text{CeO}_2$  and  $\text{TiO}_2$ , and  $\text{FeO}$  is a component of enhancing the absorption power of heat rays.

Where the total iron oxide ( $\text{T-Fe}_2\text{O}_3$ ) content is within the range of from 0.40 to 0.90%, the  $\text{FeO/T-Fe}_2\text{O}_3$  ratio is preferably from 0.27 to 0.40 in order to obtain a desired total solar energy absorbing power. The  $\text{FeO}$  content used in this ratio is usually expressed in terms of  $\text{Fe}_2\text{O}_3$  content.

In order to obtain a desired ultraviolet absorption effect with the above-described ratio of total iron oxide content and  $\text{FeO/T-Fe}_2\text{O}_3$ , it is necessary for the  $\text{CeO}_2$  content to be in the range of from 1.0 to 2.0%. If the  $\text{CeO}_2$  content is less than 1.0%, sufficiently high ultraviolet absorption effect cannot be obtained. On the other hand, if it exceeds 2.0%, the absorption of visible light in the short wavelength side is too large and the glass is tinted yellow, and as a result, desired visible light transmission and dominant wavelength cannot be obtained.

When the ultraviolet and infrared radiation absorbing glass has a thickness of 4.75 to 6.25 mm, the total iron oxide content is preferably 0.40 to 0.60%, and in this case, the  $\text{FeO/T-Fe}_2\text{O}_3$  ratio is preferably 0.30 to 0.40.

When the ultraviolet and infrared radiation absorbing glass has a thickness of from 3.25 to 4.25 mm, the total iron oxide content is preferably 0.60 to 0.90%, and in this case, the  $\text{FeO/T-Fe}_2\text{O}_3$  ratio is also preferably 0.30 to 0.40.

The  $\text{CeO}_2$  content is preferably 1.0 to 2.0%, and more preferably 1.45 to 2.0%.

$\text{TiO}_2$  is not an essential component, but can be added in a small amount in order to enhance the ultraviolet absorbing power, within the range of not impairing optical characteristics intended in the present invention. If the  $\text{TiO}_2$  content is large, the glass is readily tinted yellowish. Therefore, the upper limit of the  $\text{TiO}_2$  content is 1.0%, preferably 0.3%, and more preferably 0.15%.

The glass having the above-described composition may further contain other coloring components, such as  $\text{CoO}$ ,  $\text{NiO}$ ,  $\text{MnO}$ ,  $\text{V}_2\text{O}_5$  or  $\text{MoO}_3$ , and  $\text{SnO}_2$  as a reducing agent individually or in combination of two or more thereof in a total amount of 0 to 1%, so long as green tint intended in the present invention is not impaired. In particular,  $\text{CoO}$  gives a blue tint and is therefore effective in preventing the glass color from being tinted yellow due to increase in the amounts of  $\text{Fe}_2\text{O}_3$ ,  $\text{CeO}_2$  or  $\text{TiO}_2$ . The amount of  $\text{CoO}$  added is preferably 3 to 20 ppm.

$\text{SO}_3$  is a component that a sulfur content in the sulfur-containing materials such as salt cake added to the raw materials remains in the glass as an oxide. The  $\text{SO}_3$  content specified in the present invention plays an important role.

In the production of an ultraviolet and infrared radiation absorbing glass which is required to have an increased degree of reduction more than usual while containing a relatively large amount of  $\text{Fe}_2\text{O}_3$  or  $\text{CeO}_2$  which shows an oxidizing power as in the present invention, undissolved quartz sand aggregates (so-called scum) or reams having a large silica content (so-called silica-rich ream) tend to be formed as described above. In order to prevent such a phenomenon, the glass must have an  $\text{SO}_3$  content of 0.07% or more in order to accelerate the melting of quartz sand. This can be achieved by increasing the amount of salt cake added to the batch to, for example, about 20 Kg or more per 1 ton of quartz sand or by adding other sulfates such as iron sulfate as a raw material.

However, increase of the  $\text{SO}_3$  content in the glass in turn causes another problem such as generation of bubbles due to reboiling, particularly reboiling due to stirring with a stirrer. This reboiling phenomenon tends to occur as the  $\text{SO}_3$  content increases. Accordingly, in order to prevent reduction in the yield due to the reboiling phenomenon, the  $\text{SO}_3$  content in the glass must be 0.18% or less, and preferably 0.14% or less.

Further, for adjusting the  $\text{SO}_3$  content in the glass to fall within the above-described preferred range in order to prevent generation of scum or silica-rich reams and bubbles due to reboiling while ensuring a desired degree of reduction for the glass, a sulfide ion-containing material (for example, a sulfide such as iron sulfide, or a blast furnace slag such as Calmite produced by Calmite Co., Ltd. and Rivermite produced by Kawatetsu Kogyo KK) is preferably used as a raw material.

The present invention is described in greater detail below by referring to the Examples, but it should be understood that the present invention is not construed as being limited thereto. Unless otherwise indicated, all parts, percents, ratios and the like are by weight.

## EXAMPLES 1 TO 9

A typical soda-lime-silica glass batch component comprising by wt% of said batch component:  $\text{SiO}_2$  71.1%;  $\text{Al}_2\text{O}_3$  1.6%;  $\text{MgO}$  3.3%;  $\text{CaO}$  8.9%;  $\text{Na}_2\text{O}$  14.4%; and  $\text{K}_2\text{O}$  0.7% was appropriately compounded with ferric oxide, iron sulfide or blast furnace slag, titanium oxide and cerium oxide so as to have composition shown in Table 1 below. A carbonaceous reducing agent was appropriately further added to the resulting mixture. The mixed batch was melted in an electric furnace at 1,500°C for 4 hours. The molten glass was cast on a stainless steel plate and annealed to obtain glass samples each having a thickness of about 10 mm. Each glass obtained was polished to have a thickness of 5 mm or 4 mm. A visible light transmission (YA) measured with the CIE standard illuminant A, a total solar energy transmission (TG), an ultraviolet transmission (Tuv) defined by ISO, a dominant wavelength (DW) measured with the CIE standard illuminant C and an excitation purity (Pe) were measured as optical characteristics of each glass.

$\text{SO}_3$  content, total iron oxide (T- $\text{Fe}_2\text{O}_3$ ) content, FeO (in terms of  $\text{Fe}_2\text{O}_3$ )/T- $\text{Fe}_2\text{O}_3$  ratio,  $\text{TiO}_2$  content, and  $\text{CeO}_2$  content in the glasses obtained and optical characteristics thereof are shown in Table 1 below. In Table 1, the contents are all % by weight of the glass.

TABLE 1

	Examples								
	1	2	3	4	5	6	7	8	9
$\text{SO}_3$ (wt%)	0.08	0.12	0.12	0.10	0.09	0.12	0.12	0.10	0.10
T- $\text{Fe}_2\text{O}_3$ (wt%)	0.50	0.55	0.55	0.63	0.50	0.55	0.60	0.62	0.62
FeO/T- $\text{Fe}_2\text{O}_3$ (wt%)	0.35	0.30	0.30	0.33	0.35	0.30	0.30	0.33	0.33
$\text{TiO}_2$ (wt%)	0.03	0.10	0.13	0.25	0.10	0.25	0.03	0.12	0.25
$\text{CeO}_2$ (wt%)	1.40	1.50	1.50	1.70	1.60	1.50	1.65	1.65	1.65
Thickness (mm)	5.0	5.0	5.0	5.0	5.0	5.0	4.0	4.0	4.0
YA (%)	74.5	75.2	74.9	71.7	73.4	73.6	74.6	73.9	72.8
TG (%)	47.5	48.3	48.1	43.1	46.6	47.0	48.1	46.8	45.9
Tuv (%)	9.2	7.7	8.5	5.6	8.1	7.0	9.2	8.6	7.9
Dw (nm)	497	501	505	518	508	515	505	512	520
Pe (%)	2.9	2.1	1.9	2.6	2.2	1.7	2.5	2.3	2.1

As is apparent from Table 1, the glass samples of the Examples each having a thickness of 5 mm or 4 mm, had optical characteristics such that the visible light transmission measured with CIE standard illuminant A is 70% or more, the total solar energy transmission is less than 50%, the ultraviolet transmission is less than 10% and the dominant wavelength measured with CIE standard illuminant C is 495 to 535 nm.

## EXAMPLES 10 TO 12 AND COMPARATIVE EXAMPLES 1 AND 2

Glasses of Examples 10 to 12 were prepared by appropriately changing the amounts of salt cake, carbonaceous reducing agent, iron sulfide and the like in the bath of the glass sample of Example 8. Those glass had an  $\text{SO}_3$  content as shown in Table 2 below. Generation of scum and reboiling tendency were evaluated. The results obtained are shown in Table 2 below.

Further, glass samples of Comparative Examples 1 and 2 were prepared, which had an  $\text{SO}_3$  content fallen outside the scope of the present invention, as shown in Table 2 below. The results of evaluation on the generation of scum and the reboiling phenomenon are also shown in Table 2 below.

The glass samples of Examples 10 to 12 and Comparative Examples 1 and 2 were the same as the sample of Example 8 with respect to the total iron oxide (T- $\text{Fe}_2\text{O}_3$ ) content, the FeO (in terms of  $\text{Fe}_2\text{O}_3$ )/T- $\text{Fe}_2\text{O}_3$  ratio, the  $\text{TiO}_2$  content and the  $\text{CeO}_2$  content.

The generation of scum was evaluated by roughly classifying the amount of quartz sand come out on the surface of the melted solution when 50 g of batch was placed in a 200 ml platinum crucible and melted in an electric furnace at 1,450°C for 10 minutes, as follows.

- O: Area of quartz sand covering the surface of the melt is approximately less 20%  
 Δ: Area of quartz sand covering the surface of the melt is approximately 20 to 50%  
 X: Area of quartz sand covering the surface of the melt is approximately more than 50%.

The reboiling tendency was evaluated by placing the glass obtained after melted in a crucible, on a platinum tray, melting it at 1,300°C and examining whether bubbles are generated during melting.

TABLE 2

	SO <sub>3</sub> Content (%)	Generation of Scum	Reboiling Phenomenon
Example 8	0.10	○	Almost no occurrence
Example 10	0.06	Δ	Almost no occurrence
Example 11	0.13	○	Almost no occurrence
Example 12	0.16	○	Slightly occurred
Comparative Example 1	0.05	x	Almost no occurrence
Comparative Example 2	0.21	○	Occurred

In samples of Examples 8 and 10 to 12 having an SO<sub>3</sub> content within the scope of the present invention, the amount of scum generated was small and the reboiling tendency was slight as compared with samples of Comparative Examples, although the amount of scum generated was slightly increased in the sample of Example 9 having a smaller SO<sub>3</sub> content. On the other hand, in the sample of Comparative Example 1 having an SO<sub>3</sub> content lower than the lower limit of the present invention, a large amount of scum were generated and in the sample of Comparative Example 2 having an SO<sub>3</sub> content larger than the upper limit of the present invention, the scum was slightly generated, but the reboiling was readily occurred.

As described in detail above, according to the ultraviolet and infrared radiation absorbing glass and the production process thereof of the present invention, a green-tinted ultraviolet and infrared absorbing glass having an excellent ultraviolet and infrared radiation absorbing power, particularly, excellent ultraviolet absorbing capability, can be produced without yellowing the tint.

Further, according to the production process of the present invention, a green-tinted ultraviolet and infrared radiation absorbing glass can be produced in a high productivity without incurring problems on the production, such as generation of scum, silica-rich reams or reboiling.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

## Claims

1. An ultraviolet and infrared radiation absorbing glass comprising, in % by weight of said glass:

basic glass components comprising

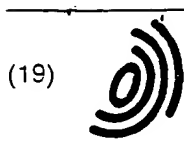
65 to 80% SiO<sub>2</sub>,  
 0 to 5% Al<sub>2</sub>O<sub>3</sub>,  
 0 to 10% MgO,  
 5 to 15% CaO,  
 10 to 18% Na<sub>2</sub>O,  
 0 to 5% K<sub>2</sub>O,  
 5 to 15% MgO + CaO,  
 10 to 20% Na<sub>2</sub>O + K<sub>2</sub>O,  
 0 to 5% B<sub>2</sub>O<sub>3</sub>, and  
 SO<sub>3</sub>, and

coloring components,  
 characterised in that the SO<sub>3</sub> is present in the range of 0.07 to 0.18%, and in that the coloring components comprise in wt% of said glass

0.40 to 0.90% total iron oxide (T-Fe<sub>2</sub>O<sub>3</sub>) in terms of Fe<sub>2</sub>O<sub>3</sub>,  
 1.0 to 2.0% CeO<sub>2</sub>; and  
 0 to 1.0% TiO<sub>2</sub>.

with 27 to 40% of said T-Fe<sub>2</sub>O<sub>3</sub> being FeO in terms of Fe<sub>2</sub>O<sub>3</sub>.

2. The ultraviolet and infrared radiation absorbing glass as claimed in claim 1, wherein the SO<sub>3</sub> content is 0.07 to 0.14%.
3. The ultraviolet and infrared radiation absorbing glass as claimed in claim 1 or 2, wherein the total iron oxide (T-Fe<sub>2</sub>O<sub>3</sub>) content in terms of Fe<sub>2</sub>O<sub>3</sub> is 0.40 to 0.60%, when said ultraviolet and infrared radiation absorbing glass has a thickness of 4.75 to 6.25 mm.
4. The ultraviolet and infrared radiation absorbing glass as claimed in claim 1 or 2, wherein the total iron oxide (T-Fe<sub>2</sub>O<sub>3</sub>) content in terms of Fe<sub>2</sub>O<sub>3</sub> is 0.60 to 0.90%, when said ultraviolet and infrared radiation absorbing glass has a thickness of from 3.25 to 4.25 mm.
5. The ultraviolet and infrared radiation absorbing glass as claimed in any one of claims 1 to 4, wherein said CeO<sub>2</sub> content is 1.45 to 2.0%.
6. The ultraviolet and infrared radiation absorbing glass as claimed in any one of claims 1 to 5, wherein 30 to 40% of said T-Fe<sub>2</sub>O<sub>3</sub> is FeO in terms of Fe<sub>2</sub>O<sub>3</sub>.
7. The ultraviolet and infrared radiation absorbing glass as claimed in any one of claims 1 to 6, wherein the glass has a visible light transmission determined with CIE standard illuminant A of 70% or more, a solar energy transmission of less than 50%, an ultraviolet transmission defined by ISO (International Organization for Standardization) of 10% or less, and a dominant wavelength determined with CIE standard illuminant C of from 495 to 535 nm, when said ultraviolet and infrared radiation absorbing glass has a thickness of from 3.25 to 6.25 mm.



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 867 415 A3

(12)

## EUROPEAN PATENT APPLICATION

(88) Date of publication A3:  
23.06.1999 Bulletin 1999/25

(51) Int Cl.<sup>6</sup>: C03C 4/08, C03C 4/02,  
C03C 3/095

(43) Date of publication A2:  
30.09.1998 Bulletin 1998/40

(21) Application number: 98302263.3

(22) Date of filing: 25.03.1998

(84) Designated Contracting States:  
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE  
Designated Extension States:  
AL LT LV MK RO SI

- Takatsuki, Nobuyuki  
Chuo-ku, Osaka-shi, Osaka (JP)
- Kuroda, Isamu  
Chuo-ku, Osaka-shi, Osaka (JP)

(30) Priority: 26.03.1997 JP 7302597

(71) Applicant: NIPPON SHEET GLASS CO. LTD.  
Chuo-ku Osaka-shi Osaka-fu (JP)

(74) Representative: Carpenter, David et al  
MARKS & CLERK,  
Alpha Tower,  
Suffolk Street Queensway  
Birmingham B1 1TT (GB)

(72) Inventors:  
• Nagashima, Yukihiro  
Chuo-ku, Osaka-shi, Osaka (JP)

(54) Ultraviolet and infrared radiation absorbing glass

(57) An ultraviolet and infrared radiation absorbing  
glass is disclosed, comprising, in % by weight:  
basic glass components comprising

65 to 80% SiO<sub>2</sub>,  
0 to 5% Al<sub>2</sub>O<sub>3</sub>,  
0 to 10% MgO,  
5 to 15% CaO,  
10 to 18% Na<sub>2</sub>O,  
0 to 5% K<sub>2</sub>O,  
5 to 15% MgO + CaO,  
10 to 20% Na<sub>2</sub>O + K<sub>2</sub>O,

0 to 5% B<sub>2</sub>O<sub>3</sub>, and  
SO<sub>3</sub>, and

coloring components comprising

0.40 to 0.90% total iron oxide (T-Fe<sub>2</sub>O<sub>3</sub>) in terms of  
Fe<sub>2</sub>O<sub>3</sub>,  
1.0 to 2.0% CeO<sub>2</sub>, and  
0 to 1.0% TiO<sub>2</sub>,

with 27 to 40% of said T-Fe<sub>2</sub>O<sub>3</sub> being FeO in terms of  
Fe<sub>2</sub>O<sub>3</sub>. The SO<sub>3</sub> is present in the range of 0.07 to 0.18%.

EP 0 867 415 A3





European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number  
EP 98 30 2263

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document: with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	EP 0 709 344 A (ASAHI GLASS CO LTD) 1 May 1996 * page 2, line 44 - line 56 * * examples 1-6,9 *	1-7	C03C4/08 C03C4/02 C03C3/095
Y,D	& JP 08 208266 A ---	1-7	
Y	JP 04 310539 A (ASAHI GLASS CO LTD) 2 November 1992 * table *	1-7	
Y	WO 91 07356 A (LIBBEY OWENS FORD CO) 30 October 1991 * page 17, line 32 - line 43 *	1-7	
Y,D	& JP 06 088812 B ---		
Y	EP 0 469 446 A (PPG INDUSTRIES INC) 5 February 1992 * example 1 *	1-7	
Y,D	& JP 04 231347 A ---	1-7	
Y,D	JP 06 056466 A (ASAHI GLASS CO LTD) 1 March 1994 * page 4, column 6, line 46 - page 5, column 7, line 10 *	1-7	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C03C
P,X	PATENT ABSTRACTS OF JAPAN vol. 098, no. 003, 27 February 1998 -& JP 09 295829 A (ASAHI GLASS CO LTD), 18 November 1997 * abstract *	1-7	
P,X	PATENT ABSTRACTS OF JAPAN vol. 098, no. 003, 27 February 1998 -& JP 09 295828 A (KOA GLASS KK), 18 November 1997 * abstract *	1-7	
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 21 April 1999	Examiner Somann, K
CATEGORY OF CITED DOCUMENTS X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &: member of the same patent family, corresponding document			



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 98 30 2263

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 012, 25 December 1997 -& JP 09 208254 A (CENTRAL GLASS CO LTD), 12 August 1997 * abstract *	1-7	
A	--- EP 0 565 835 A (GUARDIAN INDUSTRIES) 20 October 1993 * the whole document *	1-7	
A,D	& JP 07 121815 B	1-7	
A	--- EP 0 598 305 A (PPG INDUSTRIES INC) 25 May 1994 * the whole document *	1-7	
A,D	& JP 06 191881 A -----	1-7	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
Place of search MUNICH		Date of completion of the search 21 April 1999	Examiner Somann, K
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 30 2263

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

21-04-1999

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0709344	A	01-05-1996	AU 696443 B	10-09-1998
			AU 3441595 A	09-05-1996
			CA 2161379 A	27-04-1996
			CN 1128737 A	14-08-1996
			DE 69507421 D	04-03-1999
			JP 8208266 A	13-08-1996
			US 5723390 A	03-03-1998
			ZA 9509079 A	22-05-1996
-----				
JP 04310539	A	02-11-1992	NONE	
-----				
WO 9107356	A	30-05-1991	US 5077133 A	31-12-1991
			AU 629086 B	24-09-1992
			AU 6885491 A	13-06-1991
			BG 60862 B	31-05-1996
			CA 2029987 A	17-05-1991
			CN 1052647 A,B	03-07-1991
			CZ 9005665 A	12-06-1996
			EP 0453551 A	30-10-1991
			HU 66616 A,B	28-12-1994
			IE 63124 B	22-03-1995
			JP 3187946 A	15-08-1991
			JP 6088812 B	09-11-1994
			PT 95898 A,B	13-09-1991
			RU 2067559 C	10-10-1991
			PL 167809 B	30-11-1995
-----				
EP 0469446	A	05-02-1992	US 5240886 A	31-08-1993
			AT 135670 T	15-04-1996
			AU 623303 B	07-05-1992
			AU 8140491 A	06-02-1992
			CA 2048061 A,C	31-01-1992
			DE 69118042 D	25-04-1996
			DK 469446 T	22-07-1996
			ES 2087187 T	16-07-1996
			GR 3020136 T	31-08-1996
			JP 2086236 C	23-08-1996
			JP 4231347 A	20-08-1992
			JP 8000716 B	10-01-1996
			KR 9402024 B	14-03-1994
			MX 173588 B	16-03-1994
			US 5385872 A	31-01-1995
			US 5593929 A	14-01-1997
-----				
JP 06056466	A	01-03-1994	NONE	
-----				

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 30 2263

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

21-04-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0565835 A	20-10-1993	US 5214008 A	25-05-1993
		AU 3319093 A	21-10-1993
		BR 9301559 A	26-10-1993
		CA 2085264 A,C	18-10-1993
		CN 1077438 A,B	20-10-1993
		CZ 9300600 A	16-11-1994
		HU 68637 A,B	28-07-1995
		JP 6166536 A	14-06-1994
		JP 7121815 B	25-12-1995
		MX 9301842 A	28-02-1994
		NZ 247433 A	27-09-1994
		PL 298501 A	10-01-1994
		RU 2094402 C	27-10-1997
		SK 33193 A	10-11-1993
		ZA 9302086 A	15-10-1993
EP 0598305 A	25-05-1994	US 5593929 A	14-01-1997
		AT 151060 T	15-04-1997
		AU 655126 B	01-12-1994
		AU 5035693 A	26-05-1994
		BR 9304509 A	17-05-1994
		CA 2109059 A,C	14-05-1994
		CN 1087612 A,B	08-06-1994
		DE 69309398 D	07-05-1997
		DE 69309398 T	23-10-1997
		DK 598305 T	13-10-1997
		ES 2102580 T	01-08-1997
		GR 3023831 T	30-09-1997
		JP 6191881 A	12-07-1994
		JP 8000717 B	10-01-1996
		KR 9610584 B	06-08-1996
		NZ 248851 A	21-12-1995

EP 0 867 415 A3

For more details about this annex see Official Journal of the European Patent Office, No. 12/92